



## Project Summary

# Interim Protocol for the Automated Analysis of Semivolatile Organic Compounds by Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry

Donald F. Gurka

A GC/FT-IR protocol is described which is applicable to the determination of semivolatile organic compounds in wastewater, soils, sediments and solid wastes. The protocol is designed for the high-throughput automated analysis of multicomponent environmental and hazardous waste extracts. Wastewater analysis for semivolatile organic compounds is based upon extracting 1 L of sample with methylene chloride and concentrating the extract to 1 mL. The analysis of the semivolatile fraction derived from solid waste is based upon extracting 50 grams of sample and concentrating the sample extract to 1.0 mL. A gel permeation option is included to further purify those extracts that cannot be concentrated to the specified final volume. Using capillary GC/FT-IR techniques, wastewater identification limits of 150 to 400 ppb can be achieved with this method while the corresponding identification limits for solid samples are 3 to 8 ppm. Automated packed column GC/FT-IR identification limits are approximately a factor of five higher than the corresponding capillary GC/FT-IR values. The most frequent obstacle to achieving these identification limits is expected to be the presence of large quantities of interfering high boiling co-extractants. These co-extract-

ants would raise the identification limits by preventing the concentration of extracts to the desired final volume, thereby necessitating gel permeation cleanup, and/or by decreasing the spectral signal-to-noise of GC-volatile analytes by raising the spectral background intensity.

*This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The applicability of the gas chromatography/Fourier transform infrared (GC/FT-IR) spectrometric technique to the analysis of wastewater, soils, sediments, hazardous wastes, and diesel particulates has been demonstrated. Although this technique is currently one to two orders of magnitude less sensitive than gas chromatography/mass spectrometry (GC/MS), with sufficient extract concentration, GC/FT-IR is capable of detecting about 75 percent of the GC/MS detectable analytes. The scope of current GC/MS confirmatory techniques is currently limited by the availability of suitable GC

retention time standards; however, suitable spectral confirmatory techniques, such as GC/FT-IR, could eliminate this problem. However, general acceptance of the GC/FT-IR technique as a routine monitoring tool has been hindered by the lack of validated analytical protocols which provide data of known precision and accuracy.

## Conclusions and Recommendations

The analytical protocol described is adequate for the identification of environmental contaminants at the mid ppb to low ppm range. The principal problem in applying this protocol to environmental samples is expected to be the concentration of solid waste extracts to 1 mL. In these cases, the extract may be cleaned up by gel permeation or the analyst may settle for higher identification limits.

Computer software is required to determine real-time relative IR peak intensities. This software is required to provide relative intensity, as well as frequency precision, acceptance criteria for analyte identification. In addition, a consensus is required from the spectroscopic community on suitable chemical candidates for vapor-phase frequency calibration of the GC/FT-IR system (one reviewer has suggested indene for this role). This consensus should be sought from the Coblenz Society and/or the appropriate American Society for Testing Materials (ASTM) committee.

Finally, the minimum identifiable quantities of typical environmental contaminants should be determined in a round-robin study. This study should employ laboratories equipped with different model GC/FT-IR systems. This study is necessary because there are currently 11 commercial suppliers of FT-IR spectrometers. The round-robin study should be coordinated through the appropriate ASTM and/or Coblenz Society Committees.

## Results and Discussion

The minimum identifiable quantity (MIQ) of 54 environmentally important compounds using on-line GC/FT-IR techniques have been determined. The capillary GC/FT-IR MIQ's range from 300 ng of molecules with oxygen containing functional groups to 800 nanograms (ng) of the polynuclear aromatics fluorene and phenanthrene. This corresponds to a sample sensitivity of 150 to 400 parts per billion (ppb) for wastewater, if 1 L of water is extracted and the extract concentrated to 1 mL with 2  $\mu$ L of extract analyzed. A 50

gram (gm) solid sample undergoing workup by the method described in an appendix to the final report which provides sample sensitivities ranging from 3 to 8 ppm. All MIQ's were determined using the same GC program. As a result the GC peak volumes (elution volumes) of every analyte were not optimized. For example, Gurka et al. report a factor of 4.5 difference in GC peak volumes between tetrachloroethylene and di-n-butyl phthalate using the same GC program. Although large GC/FT-IR peak volumes mean reduced sensitivity via analyte dilution, multicomponent analysis necessitates that the elution volume of each analyte cannot be optimized with a single GC run. This resulting sacrifice in sensitivity is made to ensure higher sample throughputs.

These minimum identifiable quantities were obtained with the Environmental Monitoring Systems Laboratory, Las Vegas, Nevada (EMSL-LV), GC/FT-IR system, which has been described elsewhere, and has recently been updated to include a Data General Nova 4 computer equipped with a high speed array processor and a Lark Model, Control Data 50 megabyte double disk drive. GC/FT-IR sensitivity values for strong infrared absorbers ranging between 200 ng for single beam and 50 ng for double beam systems have been reported by Griffiths. However, dual-beam GC/FT-IR systems are not commercially available at this time. Recently, a researcher at the Virginia Polytechnic Institute has reported identifiable FSCC/GC/FT-IR spectra for 40 ng of some compounds. At this time

the relative sensitivities of GC/FT-IR systems purchased from different manufacturers has not been assessed. However, the MIQ's reported in this study have been generated under routine environmental analysis conditions and should be considered as realistically obtainable.

The parameters affecting GC/FT-IR sensitivity are listed in Table 1. These fall into broad categories of spectrometer, interface, chromatographic, computer, and molecular factors. In general, the analyst has control over only the chromatographic parameters and the lightpipe temperature. In some cases the analyst may have a choice of scan rates. Reduction in sensitivity by a factor of three has been reported on heating the lightpipe from ambient temperature to 240°C but it is possible that this effect may be entirely eliminated by re-configuring the spectrometer collection optics. FSCC/GC/FT-IR has been reported to be five times more sensitive than packed column GC/FT-IR. This sensitivity gain is expected from smaller capillary column, compared to packed column, elution volumes. The relative sensitivities of GC/FT-IR systems, from different manufacturers, should be assessed via a round-robin study with standard solutions.

To establish acceptance criteria for analyte identification, real-time spectral frequency precisions were determined using the Digilab-GC/S® software.

This software determines the nominal frequency in  $\text{cm}^{-1}$  at the peak top of the most intense IR bands within each spectrum. These frequency precisions for sharp IR peaks were determined to be  $\pm 1$

Table 1. GC/FT-IR Sensitivity Parameters

Location	Nature	Effect
Spectrometer	Scan Rate	Spectral S/N ( $S/N \propto \sqrt{N_{\text{scans}}}$ )
	Source Output	Signal Intensity
	Computer	Data Treatment Capacity
	A/D Converter	Data Transmission Capacity
Interface	GC/Column Type (packed or capillary)	Analyte Concentration
	Analyte Elution Volume	Analyte Concentration
	Lightpipe temperature	Spectral S/N ( $S/N \propto \frac{1}{\text{temperature}}$ )
	Detector D*	$\propto$ Intrinsic Detector Sensitivity
	Detector Element Area (A <sub>d</sub> )	Signal Density at Detector (Noise-Equivalent-Power (NEP) = $\sqrt{A_d/D^*}$ )
	Makeup Gas Water Vapor Flow Rate	Analyte Dilution Reduces S/N Analyte Concentration
Molecule	Structure	Intensity of Absorption
	Molecular Weight	Number of Molecules
	Boiling Point	Analyte Concentration

---

cm<sup>-1</sup> or less. Thus, to report an analyte as "identified," the frequencies of the major IR bands in the analyte and library spectra should agree to at least  $\pm$ cm<sup>-1</sup> and the nominal spectral frequencies for the analyte and library spectra should be determined with the same computer software. Acceptance criteria for the relative intensities of the major IR bands in the analyte and library spectra should also be established, but at present, the necessary computer software is not available.

The wastewater and solid sample workup methods used in this protocol have been described in detail elsewhere. The wastewater workup is based on Method 625 and has been modified to include the fused silica capillary (FSCC) extract analysis method of Sauter and Betowski. The solid sample workup technique has been developed by the Battelle, Midwest and Southern Institutes. This procedure has been validated for the largest solid sample size of any currently available method. A gel permeation option has been included for those extracts which cannot be sufficiently concentrated to attain the desired detection limit.

In addition to the earlier described frequency precisions, many other quality assurance/quality control (QA/QC) procedures are incorporated within the protocol. These include criteria for the instrumental centerburst intensity as a function of temperature and spectrometer day-to-day stability. QA/QC procedures are roughly divided into the classes of Daily, Periodic, and Initial Setup checks. Daily QA/QC includes a 100 percent Line Test, Single Beam Test, Spectrometer and Mirror Align Tests, and Lightpipe and Beam Splitter protective procedures. Periodic QA/QC procedures include a detector check, frequency calibration, and capillary and packed column sensitivity tests. Initial setup QA/QC includes interferometer and detector checks, frequency calibration, an interface sensitivity check, the determination of minimum identifiable quantities of target compounds, and the preparation of a calibration plot of detector centerburst intensity versus lightpipe temperature.

---

*The EPA author **Donald F. Gurka** is with the Environmental Monitoring Systems Laboratory, Las Vegas, NV 89114.*

*The complete report, entitled "Interim Protocol for the Automated Analysis of Semivolatile Organic Compounds by Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry," (Order No. PB 85-115 186; Cost: \$8.50, subject to change) will be available only from:*

*National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650*

***Donald F. Gurka** can be contacted at:  
Environmental Monitoring Systems Laboratory  
U.S. Environmental Protection Agency  
P.O. Box 15027  
Las Vegas, NV 89114*

☆ U.S. GOVERNMENT PRINTING OFFICE: 559-016/7869

United States  
Environmental Protection  
Agency

Center for Environmental Research  
Information  
Cincinnati OH 45268

BULK RATE  
POSTAGE & FEES PAID  
EPA  
PERMIT No. G-35

---

Official Business  
Penalty for Private Use \$300